

REACTIVITY OF COALS UNDER COPROCESSING CONDITIONS

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INTRODUCTION

In the recent years greater interest has developed for processes involving coal and petroleum fractions to produce distillate fuels. Coprocessing is especially attractive as a direct liquefaction process because it involves the use of heavy petroleum fractions, so both coal and heavy petroleum resids are upgraded simultaneously. The main distinction of coprocessing from other direct liquefaction processes is that coprocessing is more complex from a chemical standpoint than direct liquefaction processes which use traditional solvents, due to the greater variety of hydrocarbons (aromatics from the coal and aliphatics from the petroleum) present in the system. Therefore, need arises for better understanding of the chemical and physical interactions during coprocessing (1).

The aim of the present study is to examine the influence of reaction conditions, coal and petroleum resid properties as well as the compatibility of the coal/petroleum resid pairs in terms of structural components on total coal conversion. Special focus will be given to the reactivity of coals and interactions of the coal and resid which lead to anisotropic coke.

EXPERIMENTAL

Five coal samples, ranging in rank from subbituminous B through high volatile A bituminous, from the Penn State Coal Sample Bank were used in this project. The coals were ground to -100 mesh and stored under nitrogen. Three petroleum resid samples were used. The West Texas (FHC-470) and Blend (FHC-571) resids were obtained from Amoco Co. and Hondo resid was obtained from Unocal. Analytical data for the coal and petroleum feedstocks are shown in Tables 1 and 2.

Prior to the reaction, the coal samples were dried to a 1% moisture under vacuum. The petroleum resid samples were used as received. A mixture of resid and coal (2.5g coal + 5g resid) was placed in a 20ml stainless steel vertical tubing bomb (microautoclave) reactor. The air was evacuated from the reactor by carefully flushing with nitrogen before pressurizing with nitrogen or hydrogen gas. The starting cold gas pressure was approximately 3.5 MPa. Reactor vessels were immersed in a fluidized sand bath which was previously preheated to 350°, 400° or 450°C and was vigorously shaken during the reaction. The reaction time was usually 30 min but some additional reactions were carried out at 15, 45, and 60 min. At the end of the reactions the microautoclave was cooled nearly instantaneously by immersing it in water.

The products were washed out from the reactor with tetrahydrofuran (THF) and separated into THF-solubles and THF-insolubles. The insoluble matter was transferred to a Soxhlet thimble and was extracted under a nitrogen atmosphere for 24 h. The THF was removed from the soluble portion in a rotary evaporator and the solid residue rinsed with acetone and pentane to remove any residual THF. Both the soluble and insoluble portions were dried under vacuum for 12 h. Total coal conversion was defined on basis of the final weight of THF-insoluble matter.

In addition to coprocessing reactions, a series of baseline experiments were performed. Thermal stability tests of the petroleum resids were carried out in order to assess the amount of THF-insoluble matter resulting from the petroleum resids directly and similarly coal was reacted alone (in the absence of a solvent) under the same reactions conditions. Unreacted (raw) coal was also extracted with THF to determine the extractable amount of coal. The amount of THF-insoluble was corrected for the amount produced from resid thermal stressing before calculating the coal conversion.

The petroleum resids were fractionated into pentane-soluble and pentane-insoluble. The pentane-solubles were analyzed by GC and, when possible, with GC-MS. The coal and the solid residue were characterized by CPMAS. The insoluble residue samples were embedded in an epoxy resin and their surfaces were polished for optical microscopy. An optical microscope with reflected polarized light was used to identify anisotropic structures in the produced solid residues.

RESULTS AND DISCUSSION

Reactions were conducted in nitrogen and hydrogen atmospheres in order to determine the influence of molecular hydrogen on coal conversion. The increase in coal conversion due to hydrogen gas was estimated by the difference of the results of coal blank (no solvent) experiments under hydrogen and nitrogen at a given temperature of reaction. These results are shown in Table 3. The first observation is that presence of hydrogen increased the conversion of the two lower rank coals more than the conversion of the higher rank coals, especially at 450° C. The lower rank coals also seem to be least sensitive to molecular hydrogen at 400° C. These results agree with the observations reported by Mochida et al. (2) that higher rank coals prefer lower temperatures, while the lower rank coals prefer higher reaction temperatures. The authors relate this to the structure of the coals and the strengths of the bonds which are inversely proportionate to the preferred reaction temperature.

We previously reported (3) the results of reactions of coal with model compound solvents. For all coals, the conversions were highest at 400° C with the exception of reactions involving pyrene. Reactions with pyrene gave the highest conversion compared to the alkylated benzenes and n-alkanes, but overall, the conversions with any solvent were better than in the absence of a solvent. Also we observed that different coals reacted differently in a hydrogen and nitrogen atmosphere in the presence of a solvent. The lower rank coals actually gave higher conversions at 400° C (and in some cases at 450° C) under nitrogen, while the higher rank coals benefited from the presence of hydrogen gas. These observations indicate that coals of different rank react differently and have different response to hydrogenation and solvation conditions. Non-donor solvents under H₂ overpressure decreased the conversion for the lower rank coals compared to the blank runs and compared to the reactions under N₂. It has been reported in the literature that lower rank coals require a better hydrogen donor especially at elevated temperatures, due to the greater number of reactive species resulting from the broken crosslinks (2) and because of the smaller size of the polyaromatic structures in these coals (4).

The results of coal conversion for the coal/resid reactions based on solubility in THF are presented in Table 4. Similarly as in the model compound studies, the coprocessing experiments yielded highest conversions at 400° C. The reactions at this temperature seem to be governed by the nature of the coal, because there is little influence of the different petroleum resids. Even between the different coals there is not significant difference at 400° C. This fact is emphasized because of the great range in results when the reaction temperature is increased to 450° C. In this case the influence of the resid feedstock is evident as well as the interactions between the coal/resid pairs. The conversions at 450° C decrease compared to the previous temperature for all coal/resid pairs

but there is obviously an influence of the resids as shown by the differences between the values in Table 4 for one coal compared to those between different coals. Figures 1 and 2 show the variation of coal conversion with temperature and coal/resid feedstock pairs.

The interactions in a coprocessing system are both physical and chemical. At 350° and 400° C the dominant effect is the dissolution of the coal particles in the solvent. At these temperatures it is predominantly a physical process because no effect of the petroleum resid (solvent) is noticed and the range of coal conversion values is small. Whether the solvent (resid) acts as a donor or a non-donor is still not a significant effect at these temperatures (5). As the temperature increases the physical dissolution of coal particles reaches a limit, and the petroleum resid undergoes chemical changes at the elevated temperature. (Note that the resids produced significant amounts of THF-insolubles only at 450° C.)

We had reported earlier (3) that the coal conversion results of the coal/resid reactions were similar to those when pyrene was in the system. This would imply that the resids act as hydrogen shuttlers. Other reported investigations indicate that indeed petroleum resids act as shuttlers rather than donors (6). The aromatic compounds present in petroleum resids can act as hydrogen shuttlers. The aromaticities of the petroleum resids used in this project, determined by NMR are shown in Table 2.

In addition to following the degree of conversion by solubility of the products in THF, optical microscopy was used to study the morphology of the solid residues. The polarized light enabled identification of isotropic versus anisotropic material. Optical microscopy of the THF-insoluble residue show that the solids are in most part isotropic when the temperature of reaction is 350° and 400° C. Anisotropic structures are detected in the solid residue from coal/resid reactions that has seen temperatures of 450° C. A closer examination of the anisotropic structures indicates that anisotropy occurs at the contact between the coal and petroleum resid particles. The resid particles surround the coal particles, which later fuse. Figure 3 shows the optical micrograph of the THF-insoluble residue obtained from reaction of PSOC 1488 subbituminous coal with Blend resid at 450° C. The lighter spots represent the anisotropic structures surrounding isotropic coal particles which are fused together. Anisotropic structures formed solely from petroleum the resid are present also. Davis et al (7) compared the THF-insoluble residue of a high volatile A and high volatile C coal and found anisotropy only in the case of the high volatile A coal. Therefore, the anisotropic structures found in the residue of the coprocessing reactions, regardless of the coal rank are attributed to the presence of the petroleum resids in the system and the coal/resid interactions.

The optical textures of the solids exhibit differences depending on the coal used in the reaction. Differences observed can be correlated to the thermoplastic properties of the coals. The higher rank coal (PSOC 1504) with a FSI of 5.5 produced solids which had pores as a result of swelling. Figure 4 shows the optical micrograph of the THF-insoluble residue obtained from reactions of PSOC 1504 with Blend resid at 400° C. The isotropic coal particles contain pores which are a result of swelling. The lower rank coal (PSOC 1488) has a FSI of 0 and does not pass through a plastic range so the solid particles under the microscope showed mostly sharp cracks as a result of devolatilization. This can be correlated with the degree of coal conversion. Namely, the coal exhibiting strong thermoplastic properties (PSOC 1504) under same reaction conditions achieves higher coal conversion than the coal that does not pass through a plastic range. These result again indicate that the structural components of the coals play an important role in the interactions during coprocessing and ultimately enhance or reduce the formation of undesirable semi-coke structures.

CONCLUSIONS

The results from coprocessing of five coals of different rank with three petroleum resids indicate that the degree of coal conversion depends on the nature of the coal as well as the nature of the resids. The conversions were optimum at 400° C where the reactions seem to be governed strongly by the coal. At temperatures up to 400° C the results indicate that the dominant effect is the dissolution of the coal particles in the solvent. The nature of the resid and especially its donor abilities, effect the conversion at temperatures higher than 400° C. The petroleum resid has undergone chemical changes above this temperature and the interactions of the coal and petroleum resids become an important factor in the conversion to light weight products. This is evident under an optical microscope where anisotropic structures were detected especially at the contact between the coal and petroleum resid particles. The morphology of the particles in the insoluble residue also indicate that thermoplastic properties of coals can be related to their reactivity under coprocessing conditions. The coal exhibiting stronger thermoplastic behavior also showed to be more reactive for coprocessing. Higher thermoplasticity is an indicator of greater mobility of structural fragments leading to higher coal conversions.

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Table 1. Analyses of Project Coals.

Coal (rank)	PSOC 1488 subB	PSOC 1498 hvCb	PSOC 1501 hvBb	PSOC 1504 hvAb	PSOC 1448 hvAb
%C (dmmf)	76.56	78.24	81.17	82.88	85.20
%H	5.27	5.50	5.32	5.86	6.12
%N	0.95	1.83	1.56	1.77	1.86
%O	17.22	14.43	11.95	9.49	6.81
FSI	0.0	0.5	2.0	5.5	8.0
max fluid.T°C	n/a	n/a	421	433	438

Table 2. Analyses of Petroleum Feedstock.

	Hondo	W. Texas FHC-470	Blend FHC-571
Oils (wt.%)	43.9	39.4	21.4
Resins	40.2	59.1	62.8
Asphaltenes	15.9	0.5	14.8
%C	83.40	86.39	83.91
%H	11.80	11.23	10.26
%S	5.10	0.68	4.8
C _{ar} (%) ^a	25.4	28.5	32.3
H _{ar} (%) ^a	8.1	8.2	9.3

^a determined by NMR

Table 3. Increase in coal conversion (wt%) by hydrogenation at three temperatures.

Coal	350°	400°	450°
PSOC 1488	5.49	5.11	11.7
PSOC 1498	4.06	1.9	7.9
PSOC 1501	1.81	3.26	1.92
PSOC 1504	2.75	1.11	3.59
PSOC 1448	4.5	3.58	2.26

Table 4. Total coal conversion for coal/resid reactions at 30 minutes.

Resids	350°	400°	450°	350°	400°	450°
	N ₂			H ₂		
	PSOC 1488					
Hondo	17.61	28.63	6.86	5.46	27.29	9.93
Blend	17.73	28.46	3.45	17.35	31.32	-13.54
W.Texas	14.81	28.87	19.31	19.95	33.03	16.99
	PSOC 1498					
Hondo	12.41	22.53	3.21	7.88	22.79	48.68
Blend	11.41	24.83	0.17	11.56	27.93	-2.7
W.Texas	9.92	23.61	21.08	16.5	26.82	12.83
	PSOC 1501					
Hondo	14.99	29.92	13.4	13.36	28.89	12.41
Blend	12.36	29.5	-0.39	14.75	31.75	20.99
W.Texas	15.2	29.51	26.91	20.89	31	25.85
	PSOC 1504					
Hondo	19.14	36.54	16.53	17.38	31.3	16.66
Blend	13.73	31.94	2.54	16.48	33.94	0.52
W.Texas	13.36	33.66	26.99	14.73	31.98	28.91
	PSOC 1448					
Hondo	17.33	31.87	14.37	16.45	36.2	15.26
Blend	16.24	33.85	-0.46	14.07	32.78	6.88
W.Texas	17.5	32.35	25.99	15.26	36.39	29.05

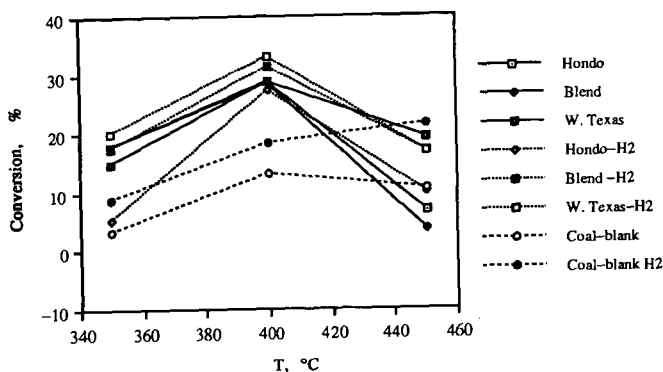


Figure 1. Coal conversion of subB coal (PSOC 1488) at three reaction temperatures under hydrogen and nitrogen atmospheres with three petroleum resid.

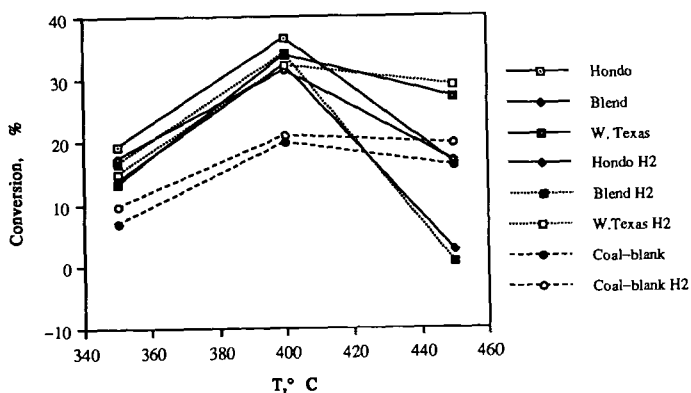


Figure 2. Coal conversion of hvAb coal (PSOC 1504) at three reaction temperatures under hydrogen and nitrogen atmospheres with three petroleum resid.

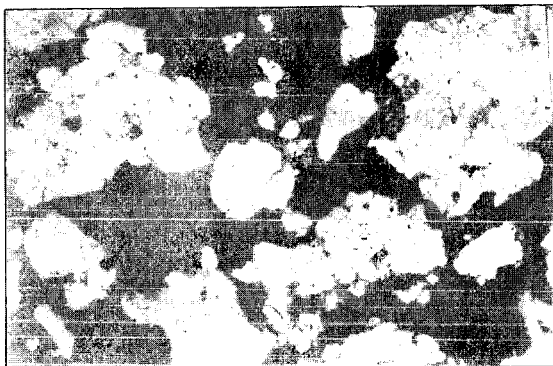


Figure 3. Optical micrograph of the THF-insoluble residue obtained from PSOC 1488 (subB) with Blend resid at 450° C.



Figure 4. Optical micrograph of the THF-insoluble residue obtained from PSOC 1504 (hVCb) with Blend resid at 450° C.